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(54) **Use of substituted 2-(2'-Hydroxyaryl)-2H-benzotriazolesulfonates as photostabilising agents for natural and synthetic fibres.**

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US-A-4 141 903
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TEXTILE RESEARCH JOURNAL, vol 38, May 1978, pages 251-255, Princeton, New Jersey, US; P.J. WATERS et al.: "The effect of phenylbenzotriazole derivatives on the photoyellowing of wool"

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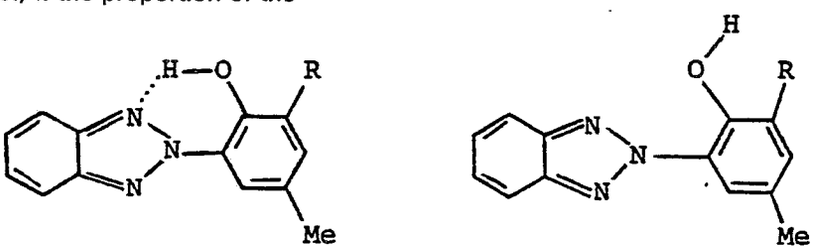
Description

This invention relates to a method for protecting synthetic and natural fibres against phototendering by the use of substituted 2-(2'-hydroxyaryl)-2H-benzotriazolesulfonates.

Phototendering is a light-induced phenomenon which manifests itself as a loss in strength and abrasion resistance of the fibre. The resultant damage is particularly noticeable in woollen car upholstery and in woollen curtains of the scrim variety, which sometimes fall apart within a few years upon exposure to sunlight — even through glass. It is of course well known that synthetic fibres and plastics are also damaged by light and it has become commonplace for additives to be added to the polymeric material before fabrication in the hope of retarding such light-induced damage. Particularly effective additives are certain organic compounds, known as ultraviolet absorbers, which absorb ultraviolet radiation preferentially thereby protecting the fibre or plastic from the damaging effects of sunlight.

The present invention had its origin in the notion that suitably modified ultraviolet absorbers might protect natural protein and synthetic fibres against phototendering. Particularly relevant to the present invention was the observation that certain sulfonic acid derivatives of substituted 2-(2'-hydroxyphenyl)-2H-benzotriazoles, a well-known class of ultraviolet absorber, reduced the rate of photoyellowing of bleached wool [Waters and Evans, *Text. Res. J., 48,* 251—255, (1978)]. Accordingly, a wide variety of benzotriazole-sulfonic acids was synthesized and applied to certain natural and synthetic fibres particularly wool, silk and nylon; their effectiveness in reducing phototendering is the subject of this invention.

The essential structural feature of 2-(2'-hydroxyphenyl)-2H-benzotriazole photostabilizers is the phenolic hydroxyl group, which is capable of forming both intra- and inter-molecular hydrogen bonds. It is the intramolecularly hydrogen-bonded form (Ia) which is responsible for the photoprotective (or photo-stabilizing) effect; if the proportion of the



Ia Ib

intermolecularly hydrogen-bonded form (Ib) is increased, as can happen in solvents [Heller, *Eur. Poly. J., Supplement* (1969), 105—132] or polymeric substrates [cf. Leaver, *J. Polym. Sci.* (Polym. Chem. Ed.) (1982), *20,* 2429] capable of disrupting the intramolecular hydrogen bond, then the photostabilizing efficiency is reduced. On the other hand, if the phenolic hydroxyl group is flanked by a bulky substituent (e.g., *t*-alkyl) located in the *ortho* position (i.e., at R), then the intramolecular hydrogen bond may be protected to some extent from the disrupting effect of hydrogen bond breaking solvents [see also Heller (reference cited above)]. Particular attention has been paid to this (possibly beneficial) bulky group effect in the research which is the subject of the present application.

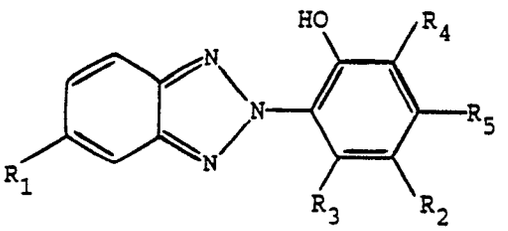
There are prior reports of the use of unsulfonated 2-(2'-hydroxyphenyl)-2H-benzotriazoles for the protection, with varying degrees of success, of some natural fibres against light e.g., mohair [van Rensburg, SAWTRI Bull., 12(4), 48—53 (1978)], cotton [van Rensburg, SAWTRI Technical Report No. 309 (1976)] and silk [e.g., Kuwahra, Nakamichi and Shoji, *Nippon Sanshigaku Zasshi, 46*(6), 486—492 (1977)]. Of particular relevance to the present invention, is the use of sulfonated 2-(2'-hydroxyphenyl)-2H-benzo-triazoles for the protection of wool against yellowing [Waters and Evans, *Text. Res. J., 48*(5), 251—255 (1978); Leaver, Waters and Evans, *J. Poly. Sci. (Poly. Chem. Ed.), 17,* 1531—1541 (1979)].

The synthesis of substituted sodium 2-(2'-hydroxyphenyl)-2H-benzotriazolesulfonates has been claimed in several recent patents (collected below). However data concerning the specific use of these sulfonates is lacking; in particular, no protection of wool, wool-blends or synthetic fibres against sunlight is disclosed. The following relevant patents are recorded:

Japanese Pat. 7,510,623 23 Apr., 1975 (Toyobo Co Ltd)
U.S. Pat. 3,849,373 19 Nov., 1974 (Du Pont de Nemours)
Swiss Pat. 615,165 15 Jan., 1980 (Ciba-Geigy)
Swiss Pat. 615,167 15 Jan., 1980 (Ciba-Geigy)
Ger. Pat. 2,835,846 22 Feb., 1979 (Ciba-Geigy)
Ger. Pat. 2,835,529 01 Mar., 1979 (Ciba-Geigy)
U.S. Pat. 4,141,903 27 Feb., 1979 (Ciba-Geigy)

It is therefore an object of the present invention to provide means to protect synthetic and natural fibres such as wool, silk and nylon from phototendering. The extension of this invention to dyed fibres is also intended.

According to the present invention there is provided a method for protecting synthetic and natural fibres against phototendering wherein the fibres are treated under acidic conditions with a substituted benzotriazole-sulfonate of the following formula:



R_1 is hydrogen or halogen, R_2 is $—SO_3X$ where X is hydrogen or an alkali metal, R_3 and R_5 are hydrogen, and R_4 is *n*-propyl, *i*-propyl, *s*-butyl, *t*-butyl, *t*-amyl or benzyl; or

R_1 is $—SO_3X$ where X is hydrogen or an alkali metal, R_2 is alkyl, R_3 and R_5 are hydrogen, and R_4 is *n*-propyl, *i*-propyl, *s*-butyl, *t*-butyl or *t*-amyl.

Preferred alkyl groups include methyl, ethyl, propyl (*n* and *i*), butyl (*s* and *t*), t-amyl and t-octyl. Preferred halogen is chlorine and preferred alkali metal is sodium.

Fibres found to be particularly amenable to the process are wool (including dyed wool), silk and nylon fibres, and blends thereof.

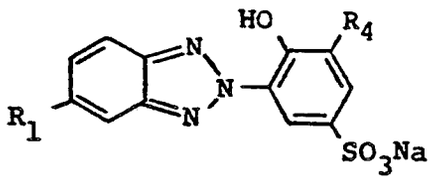
Preferred embodiments of the invention will now be described with reference to the following examples which illustrate the extent of phototendering in wool, silk and nylon samples treated with the benzotriazolesulfonates according to the invention. The extent of phototendering was measured by the breaking load found for fabric strips or yarns before and after irradiation. Unless otherwise stated in the examples, the ultraviolet absorbers (5% o.w.f.) were normally applied to the fabric at 80° for 90 minutes from an aqueous dyebath (liquor: wool ratio = 60:1) containing sulfuric acid (3% o.w.f.) and sodium sulfate (5% o.w.f.) using an Ahiba laboratory dyeing machine. Exhaustions (as measured by optical density changes of the dyebaths) ranged from 60—100% (mainly 80—100%).

Treated and control fabric samples (30 cm × 25 cm) were exposed for up to 2000 hr at a distance of 20 cm from a mercury-tungsten-phosphor lamp (Philips MBTF or ML 500W type), which is considered to provide irradiation similar to that of sunlight.

Breaking loads were determined in the weft direction on conditioned (20°; 65% r.h.) fabric strips (weft 125 mm and warp 40 mm; rate of extension 125 mm/min). The results quoted are the means of six measurements. The results are collected in eight Examples. Examples 1—7 are concerned with wool [including dyed wool (see Example 7)], and Example 8 with nylon.

Example 1

PROTECTION OF WOOL AGAINST LIGHT

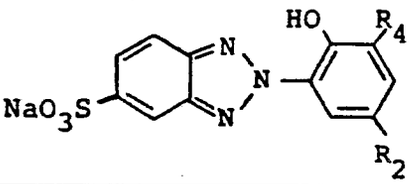


R_4	R_1	Breaking Load (lb) Before	Breaking Load (lb) After 2000 h	Strength (%) remaining after irradiation
1.1 Untreated		33.3	9.1	27.3
1.2 H	H	36.3	16.8	46.3
1.3 Me	H	43.1	22.1	51.3
1.4 Et	H	36.1	15.1	41.8
1.5 *n*-Pr	H	35.4	24.1	68.1
1.6 *i*-Pr	H	33.7	24.7	73.3
1.7 *s*-Bu	H	34.9	26.4	75.6
1.8 CH_2Ph	H	35.1	22.8	65.0
1.9 H	Cl	36.4	12.8	35.2
1.10 Me	Cl	35.9	16.6	46.2

Examples 1.5, 1.6, 1.7 and 1.8 are processes according to the invention, whereas Examples 1.1 to 1.4, 1.9 and 1.10 are comparative Examples.

Example 2

PROTECTION OF WOOL AGAINST LIGHT



R_4	R_2	Breaking Load (lb) Before	Breaking Load (lb) After 2000 h	Strength (%) remaining after irradiation
2.1 Untreated		40.5	7.5	18.5
2.2 H	Me	41.7	21.7	52.0
2.3 Me	Me	41.7	27.0	64.7
2.4 *i*-Pr	*t*-Bu	38.0	29.8	78.4
2.5 *t*-Bu	Me	41.6	35.6	85.6
2.6 *t*-Am	Me	37.6	31.8	84.6

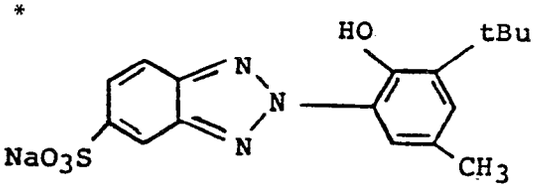
Examples 2.4, 2.5 and 2.6 are processes according to the invention whereas Examples 2.1, 2.2 and 2.3 are comparative Examples.

Example 3

PROTECTION OF WOOL AGAINST LIGHT: EFFECT OF APPLICATION pH

Sample	pH+	% Breaking Load Remaining after 2000 h
Untreated Wool	—	15.1
Control	2	15.5
+ Absorber *	2	85.6
Control	4	12.6
+ Absorber *	4	68.6
Control	5.5	12.1
+ Absorber *	5.5	53.5

*



(5% o.w.f.)

+ Exhaustion of Absorber Data: pH2 (93%); pH4 (88%); pH5.5 (76%).

Example 4

PROTECTION OF WOOL AGAINST LIGHT: EFFECT OF ABSORBER CONCENTRATION

Absorber* Concentration (% o.w.f.)	% Breaking Load Remaining after 2000 h
0	10.3
0.6	28.9
1.2	44.5
3.1	61.9
5.0	77.4

* Applied at pH2; for Formula, see Example 3

Example 5

PROTECTION OF SILK AND NYLON AGAINST LIGHT

Fabric	Treatment *	% Breaking Load Remaining
Silk[+]	None	4
	Absorber	28
Nylon 66[++]	None	16
	Absorber	67

* Absorber (3% o.w.f. used): for Formula, see Example 3
[+] Irradiated for 500 HR at 45°
[++] Irradiated for 800 HR at 45°.

Example 6

PROTECTION OF DYED WOOL AGAINST LIGHT

Treatment (or Additive)	After 1000 h at 45°		After 600 at 70°	
	BL(% RET)*	ΔE^{δ}	BL (% RET)*	ΔE^{δ}
None	29.8	8.6	19.1	21.8
Absorber[+]	67.3	1.2	55.6	10.9
Bordeaux Dye [++]	42.3	5.9	35.5	12.4
Bordeaux Dye & Absorber	60.4	4.1	50.2	6.7
Green Dye[++]	40.5	14.3	32.3	15.6
Green Dye & Absorber	60.2	7.4	41.5	9.8
Brown Dye[++]	45.8	5.2	35.7	8.6
Brown Dye & Absorber	67.9	2.0	52.7	4.3
Yellow Dye[++]	41.4	10.5	30.2	11.8
Yellow Dye & Absorber	57.3	5.7	51.5	6.8
Grey Dye[++]	37.3	6.8	29.4	10.3
Grey Dye & Absorber	53.1	3.9	49.8	6.2

* % Breaking Load Retained
[+] Absorber (2% o.w.f.) used: for Formula, see Example 3.
[++] Isolan (Bayer) Dyes used: Premetallized Azo Dyes (Lightfastness $\geq$ 6) Applied at Standard Depth.
$^{\delta}$ ΔE: Colour Difference Values, based on the CIE L,a,b colour scheme (A measure of dye fading).

The ultraviolet absorbers shown in Example 1 were prepared via direct sulfonation (with chlorosulfonic acid) of the parent benzotriazole derivatives (a typical preparation is described below).

The sulfonates shown in Example 2 where prepared by the reduction (with sodium dithionite) of the corresponding sodium *o*-nitrophenylazobenzenesulfonates (a typical preparation is described below).

In the first two examples, the first two columns of data show the breaking loads before and after irradiation; the third column shows the percentage strength remaining in the fabric after irradiation (this parameter was derived directly from the data shown in the first two columns). An assessment of the data collected in the examples leads to the following general conclusions.

(i) All the sodium benzotriazolesulfonates studied protect wool against phototendering. The degree of protection afforded increases as the percentage of sulfonate o.w.f. is increased (see Examples 4).

(ii) The pH at which the benzotriazolesulfonate is applied has an effect on its subsequent protective effect (see Example 3).

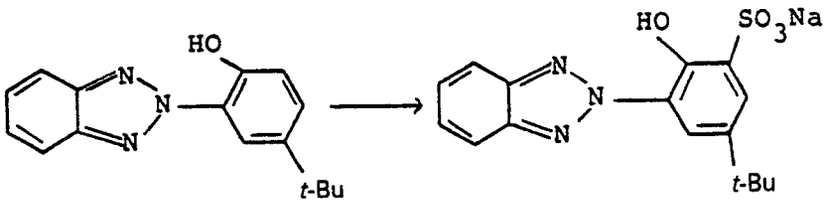
(iii) Incorporation in the process of the invention of a bulky alkyl or aralkyl group (specifically *t*-Bu, *i*-Pr, *s*-Bu, *t*-Am or benzyl) into the molecule *ortho* to the hydrogen bonded OH group increases dramatically the degree of protection obtained (see Examples 1 and 2). This result confirms the original hypothesis that such *ortho*-located bulky groups would have a beneficial effect on the degree of protection afforded by 2-(2'-hydroxyaryl)-2H-benzotriazolesulfonates.

(iv) The invention is particularly useful for dyed wool (see Example 6), the dyes [Isolans (Bayer)] being premetallised azo dyes of the sort frequently used in car upholstery. It will be seen that dyed fabrics treated with a t-butyl-benzotriazolesulfonate are protected not only against phototendering (B.L. column) but also, to some extent, against dye photofading (ΔE column). In addition to irradiation at 45° (for 1000 h), comparisons were also made for irradiations at 70°C (for 600 h), conditions under which the fabric temperature exceeds 80°C. Such a temperature is likely to be experienced by the sunlight-irradiated upholstery fabric of a car during a warm summer's day.

(v) A further study (see Example 5) showed that both silk (absorber applied at pH 2) and delustred nylon 66 (absorber applied at pH 4) were protected against phototendering by the t-butyl-benzotriazole-sulfonate.

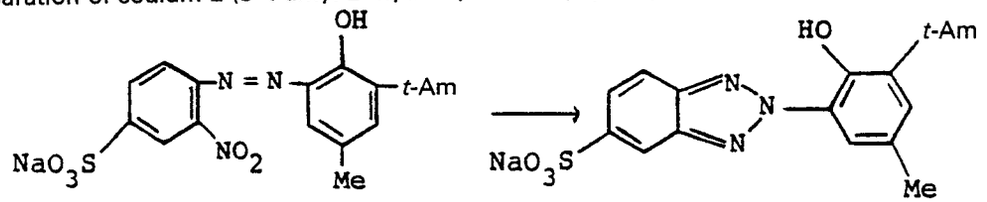
Preparation of Sodium 2-(2'-Hydroxyaryl-2H-benzotriazolesulfonates

(i) Preparation of sodium 3-(2'H-benzotriazol-2'-yl)-5-*t*-butyl-2-hydroxybenzenesulfonate



This procedure was used for all the sulfonates shown in Example 1. When chlorosulfonic acid (2.20 g; 19 mmol) was added dropwise to a warm (60°C) stirred solution of 2-(2'H-benzotriazol-2'-yl)-4-*t*-butyl-phenol (5.0 g; 19 mmol) in chlorobenzene (50 ml), a precipitate (the starting benzotriazole) was formed. However, when the temperature of the mixture was raised to the boiling point, this precipitate dissolved and, after about 10 min, a fresh precipitate (the sulfonic acid) was formed. After boiling under reflux for 2 h, the mixture was cooled, and the precipitate filtered and washed several times with hexane. This solid was dissolved in water and the solution filtered to remove some amorphous material. The filtrate was then brought to pH 7 by the addition of 10% sodium carbonate solution, and the resultant precipitate (the title sodium salt) (3.08 g) filtered, washed with ice-cold water and dried. Recrystallization from boiling water gave colourless needles. 'H n.m.r. (dimethyl sulfoxide-d_6): δ1.33, s, *t*-Bu; 7.65, d (Jc. 2Hz), H4 or H6; 7.80, d(Jc. 2Hz), H6 or H4; 11.03, s, OH. The benzotriazole ring protons were revealed as an AA'BB' pattern centred at δ7.80. The product absorbed in water at 297 and 330 nm.

(ii) Preparation of sodium 2-(3'-*t*-amyl-2'-hydroxy-5'-methyl)phenyl-5-(2H)-benzotriazolesulfonate

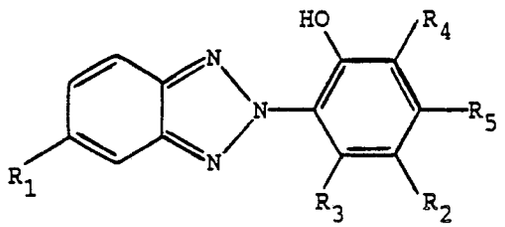


This procedure was used for the sulfonates shown in Example 2. The starting dye was prepared by coupling 4-amino-3-nitrobenzene-sulfonic acid with 2-*t*-amyl-4-methylphenol under acidic conditions [cf. Rody *et al* (Ciba-Geigy), Ger. Pat., 2,334,770 (14 March 1974); Rosevear and Wilshire, *Aust. J. Chem., 35,* 2089, 1982]. The resultant dye was isolated by bringing the pH of the mixture to 7 with 1N hydrochloric acid

and then adding salt. Some residual stickiness (due to the presence of unreacted phenol) was removed by suspending the dye in boiling hexane for 15 min. To a stirred hot (steam bath) solution of the dye (2.78 g; c. 7 mmol) in 4N sodium hydroxide (24 ml) was added dropwise a solution of sodium dithionite (not less than 85% pure) (6.3 g; 28 mmol) in water (24 ml). The initial deep purple colour of the solution was slowly replaced by an orange-yellow colour. After 3 h on the steam bath, the solution was filtered hot and the title sodium salt (1.38 g) crystallized from the filtrate as pale yellow crystals. 'H n.m.r. (dimethyl sulfoxide-d_6): δ0.67, t(Jc. 7Hz), CH_2 *CH_3* 1.42, s, $C(CH_3)_2$; 1.97, q(Jc. 7Hz), *CH_2* CH_3; 2.37, s, Ar *CH_3*; 7.17, d(Jc. 2Hz), H4'; 7.90, d(Jc. 2Hz), H6'; 11.20, vb, OH. The remaining signals could not be assigned. The product absorbed in water at 305 and 348 (inflexion) nm.

Claims

1. Method for protecting synthetic and natural fibres against phototendering wherein the fibres are treated under acidic conditions with a substituted benzotriazole-sulfonate of the following formula:



R_1 is hydrogen or halogen, R_2 is —SO_3X where X is hydrogen or an alkali metal, R_3 and R_5 are hydrogen, and R_4 is *n*-propyl, *i*-propyl, *s*-butyl, *t*-butyl, *t*-amyl or benzyl; or

R_1 is —SO_3X where X is hydrogen or an alkali metal, R_2 is alkyl, R_3 and R_5 are hydrogen, and R_4 is *n*-propyl, *i*-propyl, *s*-butyl, *t*-butyl or *t*-amyl.

2. A method as defined in claim 1, which is carried out at a pH within the range of 2—5.5 with sulphuric acid.

3. A method as defined in claim 1 or claim 2, in which the fibres are treated with the substituted benzotriazolesulfonate for about 90 minutes at about 80°C.

4. A method as defined in any one of claims 1—3, in which the liquor:fibre ratio is about 60:1.

5. A method as defined in any one of claims 1—3, in which the fibre is wool, dyed wool, silk, nylon or blends thereof.

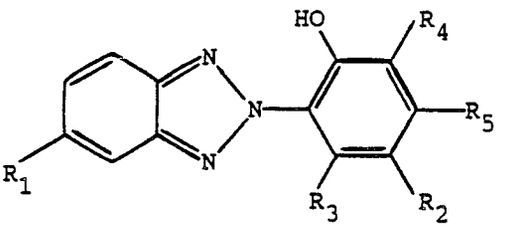
6. A method as defined in any one of claims 1—3, in which, in the formula of the substituted benzotriazolesulfonate, the halogen is chlorine and the alkali metal is sodium.

7. A method as defined in any one of claims 1—3, in which the substituted benzotriazolesulfonate is selected from the group consisting of: sodium-2-(3'-*t*-amyl-2'-hydroxy-5'-methyl)phenyl-5-(2H)-benzotriazolesulfonate; sodium 2-(3'-*t*-butyl-2'-hydroxy-5'-methyl)phenyl-5-(2H)-benzotriazolesulfonate; and sodium 2-(3'-i-propyl-2'-hydroxy-5'-*t*-butyl)phenyl-5-(2H)-benzotriazolesulfonate.

8. Fibres whenever treated with a photostabilising agent as defined in claim 1.

Patentansprüche

1. Verfahren zum Schützen von synthetischen und natürlichen Fasern gegen Schwächung durch Licht, bei welchem die Fasern unter sauren Bedingungen mit einem substituierten Benzotriazolsulfonat der nachfolgenden Formel:



behandelt werden, in welcher R_1 Wasserstoff oder Halogen ist, R_2 —SO_3X ist, worin X Wasserstoff oder ein Alkalimetall ist, R_3 und R_5 Wasserstoff sind und R_4 n-Propyl, Isopropyl, sek.-Butyl, tert.-Butyl, tert.-Amyl oder Benzyl ist; oder R_1 —SO_3X ist, worin X Wasserstoff oder ein Alaklimetall ist, R_2 Alkyl ist, R_3 und R_5 Wasserstoff sind und R_4 n-Propyl, Isopropyl, sek.-Butyl, tert.-Butyl oder tert.-Amyl ist.

2. Verfahren gemäß Anspruch 1, das bei einem pH innerhalb des Bereichs von 2 bis 5,5 mit Schwefelsäure durchgeführt wird.

3. Verfahren gemäß Anspruch 1 oder Anspruch 2, in welchem die Fasern mit dem substituierten Benzotriazolsulfonat für etwa 90 Minuten bei etwa 80°C behandelt werden.

4. Verfahren gemäß irgendeinem der Ansprüche 1 bis 3, in welchem das Verhältnis von Flüssigkeit:Faser etwa 60:1 beträgt.

5. Verfahren gemäß irgendeinem der Ansprüche 1 bis 3, in welchem die Faser Wolle, gefärbte Wolle, Seide, Nylon oder Mischungen daraus, ist.

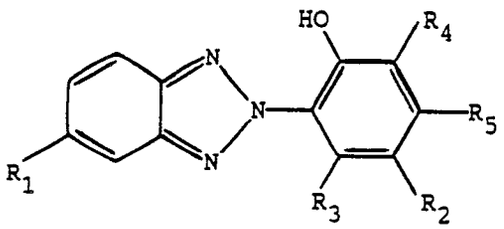
6. Verfahren gemäß irgendeinem der Ansprüche 1 bis 3, in welchem in der Formel des substituierten Benzotriazolsulfonats das Halogen Chlor und das Alkalimetall Natrium ist.

7. Verfahren gemäß irgendeinem der Ansprüche 1 bis 3, in welchem das substituierte Benzotriazolsulfonat ausgewählt ist aus der Gruppe bestehend aus: Natrium-2-(3'-tert.-amyl-2'-hydroxy-5'-methyl)-phenyl-5-(2H)-benzotriazolsulfonat; Natrium-2-(3'-tert.-butyl-2'-hydroxy-5'-methyl)-phenyl-5-(2H)-benzotriazolsulfonat; und Natrium-2-(3'-isopropyl-2'-hydroxy-5'-tert.-butyl)-phenyl-5-(2H)-benzotriazolsulfonat.

8. Fasern, sofern sie mit einem photostabilisierenden Mittel gemäß der Definition in Anspruch 1 behandelt sind.

Revendications

1. Procédé pour la protection de fibres naturelles et synthétiques contre le photo-affaiblissement, dans lequel on traite les fibres, dans des conditions acides, par un benzotriazolesulfonate substitué de formule suivante



dans laquelle

R_1 est un atome d'hydrogène ou d'halogène, R_2 est $—SO_3X$, X étant un atome d'hydrogène ou d'un métal alcalin, R_3 et R_5 sont des atomes d'hydrogène, et R_4 est un groupe n-propyle, isopropyle, sec-butyle, tert-butyle, tert-amyle ou benzyle; ou

R_1 est $—SO_3X$, X étant un atome d'hydrogène ou d'un métal alcalin, R_2 est un groupe alkyle, R_3 et R_5 sont des atomes d'hydrogène, et R_4 est le groupe n-propyle, isopropyle, sec-butyle, tert-butyle ou tert-amyle.

2. Procédé selon la revendication 1, lequel est effectué à un pH dans la plage de 2—5,5 avec de l'acide sulfurique.

3. Procédé selon la revendication 1 ou 2, dans lequel les fibres sont traitées par le benzotriazolesulfonate substitué, pendant environ 90 minutes à environ 80°C.

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel le rapport bain:fibre est environ 60:1.

5. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel la fibre est de laine, de laine teinte, de soie, de Nylon ou de mélanges de ceux-ci.

6. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel, dans la formule du benzotriazolesulfonate substitué, l'halogène est le chlore et le métal alcalin est le sodium.

7. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel le benzotriazolesulfonate substitué est choisi parmi le 2-(3'-tert-amyl-2'-hydroxy-5'-méthyl)phényl-5-(2H)-benzotriazolesulfonate de sodium, le 2-(3'-tert-butyl-2'-hydroxy-5'-méthyl)phényl-5-(2H)-benzotriazolesulfonate de sodium et le 2-(3'-isopropyl-2'-hydroxy-5'-tert-butyl)phényl-5-(2H)-benzotriazolesulfonate de sodium.

8. Les fibres traitées par un agent photostabilisant selon la revendication 1.